Conclusion

The results reported in this paper show that anions in the gas phase, like those in solution, are much less susceptible to rearrangement than are cations. Isomerizations can be induced, however, even by reaction with a water molecule. As a result, chemical methods for distinguishing isomeric structures are especially important. We have shown how a combination of reactions of D_2O, N_2O, and O_2 can be used to distinguish among isomeric allyl and cyclopropyl anions, and to follow the isomerization of allyl ions induced by water. These techniques should be of use in many other systems.

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Registry No. 1, 88377-54-2; **2**, 78427-91-5; **3**, 88377-55-3; **4**, 88377-56-4; **5**, 88377-57-5; **6**, 12558-40-6; **14**, 88377-61-1; **15**, 34172-40-2; **16**, 64066-01-9; **17**, 88377-62-2; **19**, 88377-60-0; **21**, 88377-63-3; **22**, 88377-64-4; **24**, 88377-65-5; NH_3, 7664-41-7; NH_2^-, 17655-31-1; N_2O, 10024-97-2; O_2, 7782-44-7; H_2O, 7732-18-5; CH_3OD, 1455-13-6; H_2, 1333-74-0; 1-phenyl-1-propene, 637-50-3; phenylcyclopropane, 873-49-4; 2,2-dideuteriophenylcyclopropane, 88377-58-6; 2,2-dibromophenylcyclopropane, 3234-51-3; 1-methylphenylcyclopropane, 2214-14-4; *trans*-2-methylphenylcyclopropane, 5070-01-9; 2-phenyl-1-butene, 2039-93-2; 2-phenyl-1-butanol tosylate, 88377-59-7; 2-phenylpropane, 98-83-9; 3-phenyl-1-propene, 300-57-2.

Time-Resolved Fluorescence and Absorption Spectra and Two-Step Laser Excitation Fluorescence of the Excited-State Proton Transfer in the Methanol Solution of 7-Hydroxyquinoline[1]

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Abstract: Steady-state and transient fluorescence studies of 7-hydroxyquinoline in hexane–methanol mixed solution reveal that two stoichiometric hydrogen-bonding complexes of 7-HQ and methanol (1:1 and 1:2) exhibit nearly the same wavelength fluorescences at 350–400 nm at room temperature. The 1:2 complex (N*) further exhibits a long-wavelength fluorescence at 530 nm attributable to the tautomer (T*) generated by excited-state proton transfer. The activation energy of the excited-state proton transfer of N* → T* was determined to be 0.54 kcal mol^{-1} in CH_3OH from the temperature dependence of the fluorescence rise time of T*. The transient absorption spectrum due to the ground-state tautomer (T) was observed with the lifetime of 3.5 μs, which is consistent with the recovery time (3.6 μs) of the ground-state bleaching of the absorption band. The two-step laser excitation (TSLE) fluorescence of T*, which consists of the formation of T by the first laser excitation and the second laser excitation of the T absorption band within the lifetime of T, was observed for the first time. The lifetime of T was also determined by the TSLE fluorescence intensity changes in the variable delay times of the second laser pulse from the first one. The extraordinarily large deuterium isotope effect of the T lifetime was observed in CH_3OD (τ_T = 30 μs) compared with that in CH_3OH (τ_T = 3.5 μs). The activation energy of the ground-state reaction of T → N was determined in CH_3OH (E_a = 4.2 kcal mol^{-1}) and in CH_3OD (5.5 kcal mol^{-1}) solutions by the temperature dependence of the T lifetimes determined by the variable delay technique of the TSLE fluorescence. These facts demonstrate the comprehensive mechanism of the proton transfer in the excited state as well as in the ground state and really are evidence for the intervention of the stable ground-state tautomer T in the relaxation process of T* to N.

A large number of inter- and intramolecular hydrogen-bonding systems provide us with interesting photochemical and photophysical properties of the excited-state proton transfer, which have been extensively studied by nano- and picosecond fluorescence spectroscopy. Mason et al.[2] reported that the OH group of 7- and 6-hydroxyquinolines is more acidic and the ring nitrogen atom more basic in the excited state that in the ground state. The two-stage prototropic change in the excited state from the neutral molecule to the zwitterion form was proposed to take place. Recently, Thistlethwaite and Corkill[3] have reported the picosecond fluorescence study of this excited-state proton transfer in a methanol solution of 7-hydroxyquinoline (7-HQ). They observed the excitation wavelength dependence of the fluorescence intensity ratio of the normal and zwitterion form (tautomer, T) of this compound and suggested several possible mechanisms of the excitation energy dependence of the proton transfer, including that via upper vibrational states (S_1). Very recently, Thistlethwaite[4] has reported the reexamination of this phototautomerization suggesting an important participation of the solvent methanol or ethanol molecules. On the other hand, the transient absorption study that may provide us with valuable information on the existence of the ground-state tautomer (T) and on the reverse proton transfer in the ground state reproducing the parent molecule has never been reported except for a few papers.[1,5,6] In the excited-state proton transfer of *o*-hydroxybenzophenone in ethanol, Hou et al.[7] reported a very rapid recovery of the ground state.

(1) A preliminary communication has been reported: Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 4828.
(2) Mason, S. F.; Philp, P. E. *J. Chem. Soc. A* **1968**, 3051.
(3) Thistlethwaite, P. J.; Corkill, P. J. *Chem. Phys. Lett.* **1982**, *85*, 317.
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(5) Huston, A. L.; Scott, G. W.; Gupta, A. J. *J. Chem. Phys.* **1982**, *76*, 4978.
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(7) Hou, S.-Y.; Hetherington, W. M., III; Korenowski, G. M.; Eithenthal, K. B. *Chem. Phys. Lett.* **1979**, *68*, 282.

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Recently, Huston et al.[5] have reported the ground-state absorption recovery and fluorescence decay kinetics of 2-(2-hydroxy-5-methylphenyl)benzotriazole in several solvents and suggested the intervention of an intermediate form during the excited-state relaxation process on the basis of the controversy that the fluorescence lifetime is shorter than the ground-state recovery time.

This paper presents the steady-state and transient fluorescence studies of the intermolecular excited-state proton transfer of 7-hydroxyquinoline (7-HQ) in methanol–hexane mixed solvent and in methanol solution. In the methanol solution, 7-HQ may make 1:1 and 1:2 complexes with methanol molecules in the ground state, and both complexes may show nearly the same fluorescence spectra in the 350–400-nm region. The excited-state proton transfer exhibiting the long-wavelength tautomer fluorescence (T*, λ_{max} 530 nm) takes place only from the latter complex (1:2). Therefore, the excitation energy dependence of the intensity ratio of the short- and long-wavelength fluorescence also observed here may be interpreted by this point of view. The transient absorption kinetics of the ground-state tautomer (T) generated in the excited-state proton transfer and the fluorescent relaxation in the methanol solution was determined. This paper further demonstrates the first observation of the two-step laser excitation (TSLE) fluorescence of T*. The ground-state tautomer generated in the excited-state proton transfer by the first laser excitation and the second laser excitation of the T absorption band (one to several microseconds delayed from the first one) affords the TSLE fluorescence of T*, which is identical with the oridinary fluorescence spectra in the excitation of N (1:2 complex with methanol). The lifetimes of T were determined to be 3.5 μs in CH_3OH at room temperature while ~30 μs in CH_3OD and/or CD_3OD. The extraordinarily large deuterium isotope effect of the lifetime of T are discussed in terms of the vibrational coupling between N and T forms and the difference of zero-point energy.

Experimental Section

Materials. 7-Hydroxyquinoline (Eastman Kodak) was purified by 2 times recrystallization. Spectral grade methanol (Nakarai Chem) was used without further purification, and methanol-d_1 and methanol-d_4 (both CEA 99.0%) were used after distillation in a vacuum line.

Fluorescence Lifetime and Transient Absorption Measurements. Fluorescence lifetimes were determined by a time-correlated single-photon counting system (Ortec) with a multichannel analyzer (Norland) and with a D_2 nanosecond light pulser (PRA model 510) through a monochromator (RITSU MC-10). The fluorescence was detected by a HTV 1332 photomultiplier through several appropriate band-pass and/or cutoff filters. The fluorescence decay curves were analyzed by a computer-simulated convolution. Transient absorption spectra and the ground-state bleaching and recovery were determined by using a N_2 laser (Molectron UV-12) and a monitoring Xe flash lamp (USSI 3CP-3) system reported in the previous paper.

Two-Step Laser Excitation Fluorescence Spectra and Variable Delay Technique. A home-made N_2 laser (fwhm, ~7 ns; peak power, ~500 kW; repetition rate, ~1 Hz) was used as the first excitation laser. In order to remove the effect of a jitter of the first laser pulse, a pin photodiode and a delay circuit were used for the trigger signal to operate the second N_2 laser pumped dye laser (Molectron UV-12 and DL-14). The TSLE fluorescence signal was detected by a HTV 1P28 photomultiplier, which was operated with subnanosecond response time developed by Beck.[8] The signal was determined by a Tektronix oscilloscope 7904 (7A19 and 7B85), which is triggered by the second laser pulse detected by a biplaner phototube (HTV R617-02). The two-step laser excitation fluorescence spectra were constructed with the oscilloscope signal intensities of TSLE fluorescence. The TSLE signal was confirmed by the fact that the signal cannot be detected without the first laser and also without the second one. The lifetimes of T were determined from the TSLE fluorescence signal which was detected by the second excitation pulse (440, 406, and 386 nm) at several delay times from the first laser pulse.

Results and Discussion

Steady-State and Transient Fluorescence Studies. The methanol solution of 7-HQ exhibits dual fluorescence in the 350–400-nm and 500–550-nm regions, as reported previously. However, the hexane solution is almost nonfluorescent, while the solution containing very small amount of methanol exhibits dual fluorescence.[9,10] Figure 1 shows the fluorescence spectra of 7-HQ in the hexane–methanol mixed solvent. The shorter wavelength fluorescence spectra exhibit a rather complex shift with increasing methanol concentration, while the long-wavelength fluorescence increases in intensity, as shown in Figure 1. The plots of C^{-2} vs. F^{-1}, where F is intensity of the 530-nm fluorescence and C is the concentration of methanol in hexane, exhibiting a linear relationship (shown in Figure 1) suggest that the long-wavelength fluorescence may be attributable to the 1:2 interaction of 7-HQ with CH_3OH molecules.[10] If the long-wavelength fluorescence is ascribed to the excited-state tautomer (T*) generated by the proton transfer as reported previously, two methanol molecules may be required for the long-wavelength tautomer fluorescence of 7-HQ. The excitation spectra of the dual fluorescence (λ_{max} 378 and 530 nm) exhibit a rather different spectral distribution as shown in Figure 2. The excitation spectrum of the 530-nm T* fluorescence exhibits a rather longer wavelength than that of the 350–400-nm fluorescence in the small concentration of methanol. However, with increasing methanol concentration, these

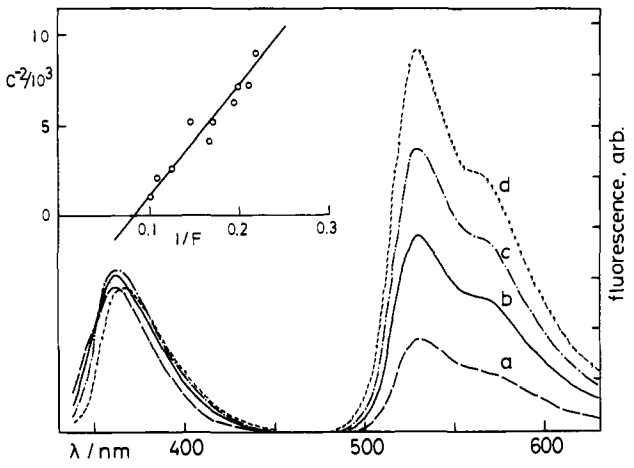


Figure 1. Fluorescence spectra of 7-HQ (5×10^{-6} M) in hexane containing CH_3OH at room temperature (~20 °C). CH_3OH concentration: (a) 0.025 M, (b) 0.035 M, (c) 0.044 M, (d) 0.10 M. The insert shows plots of C^{-2} vs. F^{-1} at this temperature where C and F are the concentration of CH_3OH and fluorescence intensity at 530 nm, respectively.

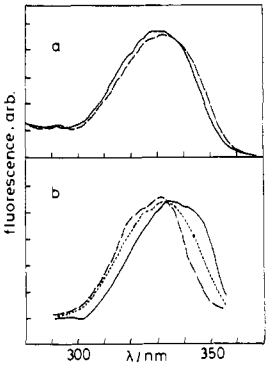


Figure 2. Fluorescence excitation spectra of 7-HQ (10^{-5} M): (a) in CH_3OH monitored at 500 nm (—) and at 378 nm (---), (b) in hexane containing CH_3OH (0.035 M) monitored at 530 (—), 390 (---), and 355 nm (---) (concentration of 7-HQ, 5×10^{-6} M). The spectra were determined at room temperature (25 °C).

(8) Beck, G. *Rev. Sci. Instrum.* **1976**, 47, 537.

(9) No long-wavelength fluorescence at 530 nm but only the short-wavelength fluorescence at 350–400 nm were observed in a very dilute methanol solution (<0.01 M) in hexane, and the ratio of the fluorescence intensity (F) at 400 nm and the methanol concentration (C), F/C, exhibits an approximately linear dependence on methanol concentration. This fact suggests that the 350–400-nm fluorescence may be attributed to a 1:1 complex between 7-HQ and CH_3OH. See ref 10.

(10) Baba, H.; Matsuyama, A.; Kokubun, H. *Spectrochim. Acta, Part A* **1969**, *25A*, 1709.

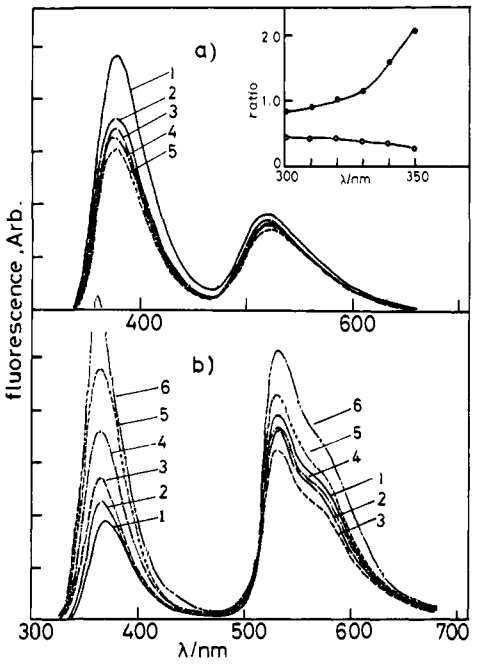
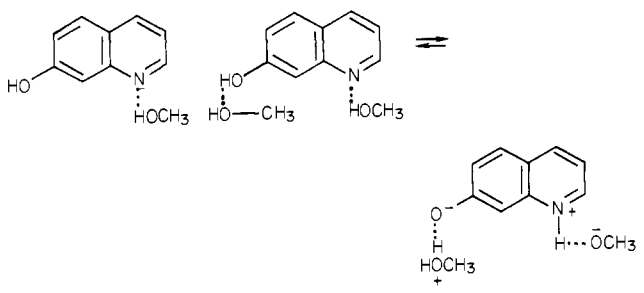


Figure 3. Excitation wavelength dependence of fluorescence spectra of 7-HQ (5×10^{-5} M): (a) in CH_3OH, (b) in hexane containing CH_3OH (concentration of 7-HQ, 5×10^{-6} M; CH_3OH concentration, 0.025 M). Excitation wavelengths: (1) 350 nm; (2) 340 nm; (3) 330 nm; (4) 320 nm; (5) 310 nm; (6) 300 nm. The inset shows plots of fluorescence intensity ratio (I_{530}/I_{378}) vs. excitation wavelength in CH_3OH (○) and in hexane-methanol (●), determined at room temperature.

two excitation spectra gradually approach each other, and the T* fluorescence excitation spectrum is at slightly shorter wavelength than that of the 350–400-nm fluorescence in methanol solution, as shown in Figure 2. These steady-state fluorescence studies suggest that the violet 350–400-nm fluorescence seems to consist of two fluorescence components of the 1:1 and 1:2 H-bonding complexes of 7-HQ with methanol molecules, while the 530-nm fluorescence may be ascribed to the tautomer (T*) generated from the 1:2 complex (N*) in the excited state. Therefore, the excitation wavelength dependence of the intensity ratio of the dual fluorescence in the methanol solution as mentioned above seems to be attributable to the existence of the two H-bonding complex fluorescence in the 350–400-nm region. This argument may be further supported by the excitation wavelength dependence of the similar intensity ratio (I_{530}/I_{378}) in the hexane–methanol mixed solvent; in contrast to the methanol solution, the intensity ratio (I_{530}/I_{378}) decreases with decreasing excitation wavelength, as shown in Figure 3. This is because the absorption band of the 1:2 H-bonding complex in small concentrations of CH_3OH seems to be at a little longer wavelength than that of the 1:1 complex. The schematic structures of these H-bonding complexes are as follows:



The potential energy diagram and the rate constants of the proton transfer in the excited state as well as in the ground state are shown in Figure 4, where N and N* are the ground and excited states of the 1:2 H-bonding complex, respectively; T and T* represent the tautomer forms in the ground and excited states,

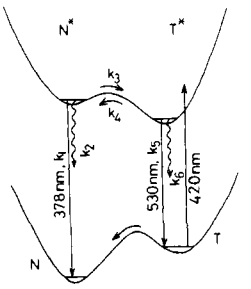


Figure 4. Potential energy diagram and rate constants of the proton transfer in the ground and excited states, and of the radiative and nonradiative processes.

Table I. Fluorescence Decay (Rise) Times (ns) of the H-Bonding Complexes of 7-HQ with CH_3OH (CH_3OD) and the Tautomer and the Decay Times (μs) of the Ground-State Tautomer

	H-bonding complex[c]		T*		T	
	1:1	1:2 (N*)	λ_1	λ_2	absorp[a]	TSLE[b]
CH_3OH	2.05	0.20	2.75	0.29	3.5	3.5
CH_3OD	3.41	0.28	7.04	0.32	24	30

[a] Determined by the transient absorption technique. [b] Determined by the variable delay technique of TSLE fluorescence.

respectively. The time-dependent concentrations of N* and T* are expressed by the well-known equations as follows:[11]

$$[N^*] = \frac{[N^*]_0}{\lambda_2 - \lambda_1}[(\lambda_2 - X)e^{-\lambda_1 t} + (X - \lambda_1)e^{-\lambda_2 t}] \quad (1)$$

$$[T^*] = \frac{k_3[N^*]_0}{\lambda_2 - \lambda_1}[e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (2)$$

where $X = k_1 + k_2 + k_3$, $Y = k_4 + k_5 + k_6$, and $\lambda_1, \lambda_2 = {}^1/_2[X + Y \mp [(X - Y)^2 + 4k_3k_4]^{1/2}]$.

The rise and decay curve of the T* fluorescence was observed in the methanol solution of 7-HQ. The double exponential decay of the 350–400-nm fluorescence was observed; the data are summarized in Table I. However, the decay times of the 350–400-nm fluorescence cannot correspond to the time constants of the rise and decay of the T* fluorescence. Since the 350–400-nm fluorescence may consist of the two types of H-bonding complex fluorescences, the time constant of 0.2 ns in the double exponential decay seems to be attributable to the decay of the 1:2 complex (N*) fuorescence, and that of 2.0 ns to the 1:1 complex. These assignments of the decay times were confirmed by the following results in the CH_3OD solution. In the CH_3OD solution of 7-HQ, the rise and decay times of the T* fluorescence were observed to be 0.32 and 7.0 ns at room temperature, respectively, and the decay times of the double exponential of the 350–400-nm fluorescence were observed to be 0.28 and 3.4 ns. Therefore, the rise time (0.29 ns) of the T* fluorescence in CH_3OH may be corresponding to the decay time (0.20 ns) of 1:2 H-bonding complex fluorescence.

The rise time of the T* fluorescence in the CH_3OH and CH_3OD solutions was measured at several temperatures. Since the 350–400-nm fluorescence consists of two components of fluorescences, the activation energy of the N* → T* cannot be determined from the fluorescence intensity ratio and T* lifetime.[12] Therefore, the activation energies of the excited-state proton transfer from N* to T* were determined to be 0.54 kcal mol^{-1} in CH_3OH and 1.9 kcal mol^{-1} in CH_3OD from the plots of the time constants of the fluorescence rise vs. $1/T$, assuming $(X - Y)^2 \gg 4k_3k_4$ (Figure 5). The unusually large deuterium isotope effect of the decay time of T* and the activation energy of excited-state proton transfer

(11) Ware, W. R.; Watt, D.; Holmes, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 7853.

(12) Itoh, M.; Tokumura, K.; Tanimoto, Y.; Okada, Y.; Takeuchi, H.; Obi, K.; Tanaka, I. *J. Am. Chem. Soc.* **1982**, *104*, 4146.

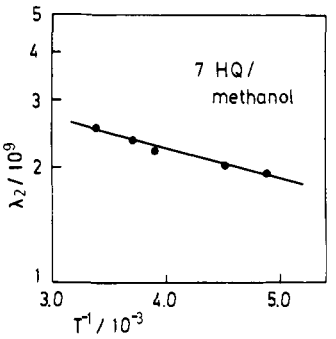


Figure 5. Plots of the rate constant of the T* fluorescence rise vs. $1/T$ (temperature) of a methanol solution of 7-HQ.

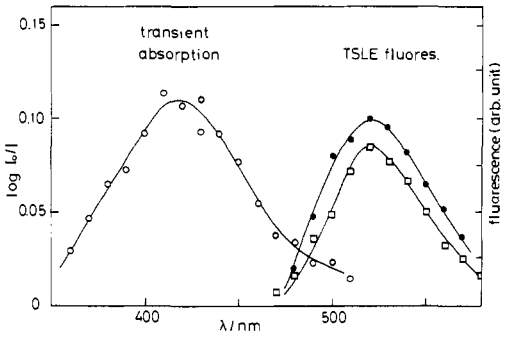


Figure 6. Transient absorption spectrum (○) of a methanol solution of 7-HQ (7×10^{-5} M) depicted at 500-ns delay after a laser pulse. The light path length is 5 mm. The TSLE fluorescence spectra of a 7-HQ solution (4.3×10^{-4} M) were excited at 440 nm (●) and at 386 nm (□) pulses at 1.2 μs delayed from the first N_2 laser pulse.

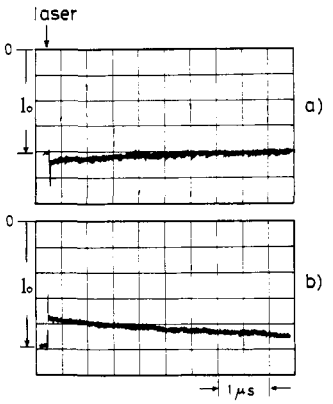


Figure 7. The oscilloscope trace of (a) the recovery of the ground-state bleaching at 340 nm of 7-HQ solution (7×10^{-5} M) in CH_3OH and (b) the decay of the transient absorption at 440 nm at room temperature: coordinates are 0.5 μs/division and ordinates are 50 mV/division.

are discussed in terms of the zero-point energy of the N* state and the vibrational coupling between two excited states.

Transient Absorption and Two-Step Laser Excitation (TSLE) Fluorescence Spectra. The transient absorption spectra and bleaching of the ground-state absorption band of the methanol solution of 7-HQ were measured at room temperature. The considerably strong absorption band was observed at ~420 nm, as shown in Figure 6. The decay time of the absorption was determined to be 3.5 μs in the aerated solution, since the decay time was observed to be almost invariant in the deaeration. Further, since the decay times of the excited species of N* and T* are as short as subnanosecond, the considerably long-lived transient absorption band may be attributed to the ground-state tautomer T generated by the excited-state proton transfer and the relaxation. This argument was evidenced by the identical recovery time (3.6 μs) of the bleaching of the ground-state absorption band, which is also invariant in the deareation. These decay curves (oscilloscope traces) of the transient absorption and

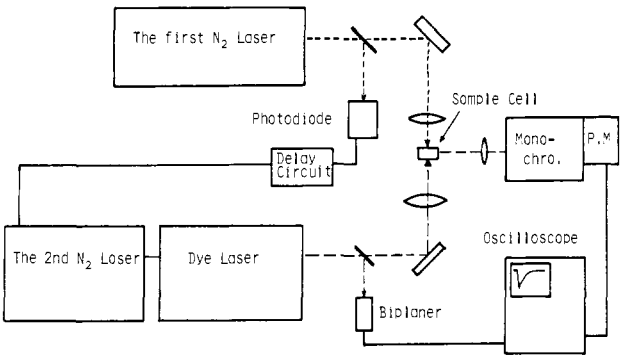


Figure 8. Experimental setup of the two-step laser excitation fluorescence.

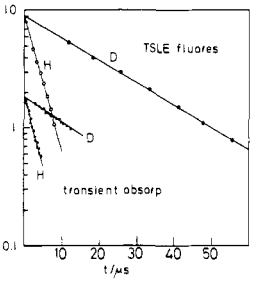


Figure 9. TSLE fluorescence intensity vs. variable delay times of the second pulse (440 nm) after the first one (337 nm) of 7-HQ in CH_3OD (●) and CH_3OH (○) and the transient absorption decay. The abscissa for the TSLE fluorescence is the delay time and that for the transient absorption is the decay time.

the recovery are shown in Figure 7. The decay time of the transient absorption of the CH_3OD solution was also determined to be 24 μs at room temperature. The decay time obtained in the CH_3OD solution exhibits an extraordinary large deuterium isotope effect. These facts demonstrate the mechanism of the ground-(T → N) and excited-state (T* ← N*) proton transfer, including the intervention of the ground-state tautomer T in the relaxation of T* to N.

If the long-lived transient absorption band of T is exclusively excited within the lifetime by the second laser pulse at several microsecond delay from the first laser excitation, the T* fluorescence spectrum should be obtained. The two-step laser excitation (TSLE) fluorescence of this solution was observed, as shown in Figure 6. The experimental setup for the TSLE fluorescence is shown in Figure 8. The TSLE fluorescence spectra are identical with the ordinary fluorescence spectra in the excitation of the N form (1:2 H-bonding complex). Further, the TSLE fluorescence spectra were independent of the excitation wavelength of the second laser pulse (440, 406, and 386 nm). The TSLE fluorescence shows a single exponential decay without a fluorescence rise, though the T* fluorescence in the excitation of N followed by the excited-state proton transfer exhibits a rise and decay, as mentioned in the preceding section. The decay times of T* are invariant with changing the second laser wavelength within the experimental error. No excitation energy dependence of the TSLE fluorescence spectra and lifetimes observed here may remove a possibility of the fluorescence relaxation from the upper vibrational states of T*, which may be produced by the excited-state proton transfer via upper vibrational states. If a reverse proton transfer in the excited state (N* ← T*) takes place via upper vibrational states of T*, the TSLE fluorescence of N* in addition to the TSLE T* fluorescence might be observed by the second laser excitation to the higher vibrational levels of T*. Unfortunately, no TSLE fluorescence of N* was detected in the second laser excitations at 386 and 406 nm, which suggests lack of the reverse proton transfer in the excited state.

If the TSLE fluorescence intensities are measured by the second laser excitation at several delay times after the first one, the decay times of T can be obtained. Figure 9 shows plots of the TSLE

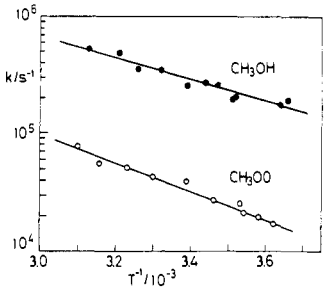


Figure 10. Plots of the decay rate constants of T in the CH_3OH solution (●) of 7-HQ and in the CH_3OD solution (○). Concentrations of 7-HQ are $\sim 5.4 \times 10^{-6}$ M in both solutions.

fluorescence intensities vs. the variable delay times of the second pulse after the first one. The decay time of T obtained from this TSLE fluorescence intensity (a variable delay technique) is almost identical with that by the transient absorption technique. Since the monitor flash lamp for the transient absorption used here has several tens of microsecond duration, it is difficult to determine the lifetimes of the long-lived transients. Therefore, the decay times of T were determined at several temperatures by the variable delay technique of the TSLE fluorescence, because the TSLE fluorescence is more sensitive and more accurate than the transient absorption. Figure 10 shows log plots of the decay constants of T in both CH_3OH and CH_3OD solutions. The activation energies (E_a) of the decay of T were obtained in CH_3OH (E_a = 4.2 kcal mol^{-1}) and in CH_3OD (5.5 kcal mol^{-1}). The activation energies of the T decay obtained may imply those of the reverse proton transfer in the ground state (T → N). The extraordinarily large deuterium isotope effect on the decay time of T and the activation energy of the proton transfer will be discussed in the following section.

Mechanism of the Proton Transfer in the Ground and Excited States. Numerous investigations have been reported on the inter- and intramolecular excited-state proton transfer.[13-17] In the intramolecular excited-state proton transfer of methyl salicylate, Smith and Kaufmann[18] reported that the closed form of this compound including intramolecular hydrogen bonding between phenol hydrogen and carbonyl oxygen atoms exhibits a rapid formation of the tautomer, while no normal form (N*) fluorescence corresponding to the tautomer was observed. The fluorescence spectrum observed in the 340-nm region, which had been assigned as the N* form corresponding to the tautomer by Weller,[13] was reported to be attributable to the different H-bonding conformer between phenol hydrogen and methoxy oxygen atoms. No excited-state proton transfer takes place in this H-bonding conformer. On the other hand, Thistlethwaite and Corkill[3] observed the dual fluorescence in the methanol solution of 7-HQ exhibiting excitation energy dependence of the fluorescence intensity ratio of this dual fluorescence, and they reported that the decay of the 383-nm fluorescence was expressed by the double exponential (τ = 0.25 and 2.25 ns), while that of the 523-nm fluorescence by the rise and decay (τ = 0.17 and 2.95 ns). If the reaction mechanism of the excited-state proton transfer is followed by an excited-state equilibrium, the rise and decay times should be almost identical with the double exponential decay (eq 1 and 2), respectively. However, there is somewhat of a discrepancy between them. Furthermore, the excitation energy dependence of the fluorescence intensity ratio of the dual fluorescence cannot be interpreted by the proton transfer via upper vibrational states,[19,20] because the observed rise time of T* fluorescence means a rather slow proton transfer which may conflict with the very rapid proton transfer and vibrational relaxation in the upper vibrational S_1 state. In a recent paper, Thistlethwaite[4] suggested the important role of the solvent molecules (CH_3OH or C_2H_5OH) in this excited-state proton transfer.

In this paper, the participation of two methanol molecules in the appearance of the T* fluorescence was shown, and further the overlapping of fluorescence spectra due to the two H-bonding species (1:1 and 1:2) of 7-HQ and methanol in the 350–400-nm region was demonstrated, though the fluorescence properties are rather complicated in the mixed solvent (hexane–methanol). The double exponential decays (τ = 2.05 and 0.2 ns) of the 350–400-nm fluorescence in CH_3OH are not ascribed to the decay times in eq 1 but to those of two H-bonding species (the former for 1:1 and the latter for 1:2 hydrogen-bonding complexes). From the fractions (A) of the fluorescence decay components, approximately 85–90% of 7-HQ in the methanol solution may be attributable to the 1:2 complex. It seems that these two H-bonding species are formed as follows: one CH_3OH molecule binds to a nitrogen atom of 7-HQ and the second CH_3OH to the phenol hydrogen atom, though the binding of the second CH_3OH to 7-HQ seems to be much smaller than that of the first one.[10] The excited-state proton transfer may take place in this 1:2 H-bonding complex. As a result, a hydrogen atom appears to transfer from the phenol group to the ring nitrogen atom.

The activation energy (E_a) of the proton transfer was determined to be 0.54 kcal mol^{-1} in the excited state by the temperature dependence of the fluorescence rise time of T*. In this determination of E_a, $(X - Y)^2 \gg 4k_3k_4$ and $k_3 \gg k_4$ were assumed. The assumption of a negligible reverse proton transfer in the excited state was confirmed by no TSLE fluorescence of N* as mentioned above. The very small activation energy of the proton transfer demonstrates almost no potential barrier for N* to T*, while no fluorescence of N* in the two-step laser excitation of the blue end (386 nm) of the T absorption band suggests a high potential barrier of the reverse proton transfer in the excited state, as shown in Figure 4. In the excited-state proton transfer of 2-(2-hydroxy-5-methylphenyl)benzotriazole, Huston et al.[5] observed a recovery time (33 ± 5 ps in cyclohexane) of the absorption band bleaching, which is considerably longer than the fluorescence decay time (14.4 ± 3.4 ps). They suggested an intervention of an intermediate form during the excited-state relaxation process. However, no transient due to the ground-state tautomer was detected. In this paper, it is noteworthy that the observation of the transient absorption band of T in 7-HQ is the first evidence of the real existence of the ground-state tautomer. Furthermore, the TSLE fluorescence spectrum of T* is the strong confirmation of the transient absorption of T in the T* relaxation process. The transient absorption band observed is in a nice mirror image to the T* fluorescence. The lifetime of T by the variable delay technique of the second pulse after the first one is identical with that determined by the transient absorption technique, which implies the complete evidence of the ground- and excited-state relationship of T. The decay rate constant of T means the reaction rate constant of the ground-state reverse proton transfer from T to N. The activation energy of this reaction was determined to be 4.2 kcal mol^{-1} by the variable delay technique of the TSLE fluorescence at several temperatures, as mentioned in the last section. The potential energy curves in Figure 4 are depicted in taking account of the activation energies of T to N and also of N* to T*.

Since the reverse proton transfer in the excited state is negligible, the deuterium isotope effect on the decay rate of T* and the activation energy of this process may be attributable to the nonradiative process of T*. Therefore, the large isotope effect

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of the T* decay time suggests that the N–H(D) vibration seems to take an important role in the nonradiative process of T*. The isotope effect of the activation energy of the excited-state proton transfer was observed to be unusually large, though the determination of activation energy from the fluorescence rise time of T* has less accuracy. The difference of the activation energy of 1.4 kcal mol^{-1} is fortunately close to the difference of the zero-point energy between O–H and O–D vibrations.[21] Furthermore, the decay constant of T and the activation energy of T to N exhibit also unusually large deuterium isotope effect. Since any photochemical reactions and any other decay processes than that to the ground-state normal form N do not seem to be involved in the decay of T, the observed deuterium isotope effect on the decay of T may be really reflected by that of the reaction rate constant of T → N. The difference of the activation energy of this reaction was estimated to be 1.3 kcal mol^{-1}, which is consistent with that of the zero-point energy of the initial state of T.[21,22] On the other hand, the isotope effect on the proton-transfer reactions in both the ground and excited states may be interpreted in terms of the nonradiative process as a vibrational coupling between the double minimum potentials of T and N (or N* and T*). This type of nonradiative process is known as an isoenergetic transition between two upper vibrational states of T and N with an activation barrier.

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Registry No. 7-Hydroxyquinoline, 580-20-1; methanol, 67-56-1; deuterium, 7782-39-0; methanol-d_1, 1455-13-6.

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Effects of Amino and Nitro Substituents upon the Electrostatic Potential of an Aromatic Ring

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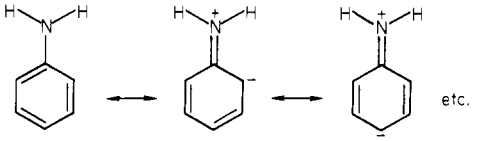
Abstract: We have calculated the electrostatic potentials of benzene, aniline, nitrobenzene, and the three isomeric nitroanilines in order to study the effects of $-NH_2$ and $-NO_2$ substituents in activating or deactivating the aromatic ring toward electrophilic attack. The potentials were computed with use of SCF STO-5G wave functions, after the molecular geometries were first optimized at the STO-3G level. (Resonance considerations are notably effective in rationalizing the changes in geometry that accompany the introduction of $-NO_2$ into aniline.) Benzene itself has extensive negative potentials (attractive toward electrophiles) above and below the aromatic ring, in the π regions. These are significantly stronger in aniline, indicating a considerable degree of activation, but are entirely eliminated in nitrobenzene. When both $-NH_2$ and $-NO_2$ are present, the deactivating influence of the latter dominates, although there remains evidence of the directing properties of $-NH_2$. An interesting feature observed in nitroaromatic potentials is a positive buildup that occurs over the C–NO_2 bond regions. This may indicate a possible pathway for nucleophilic attack.

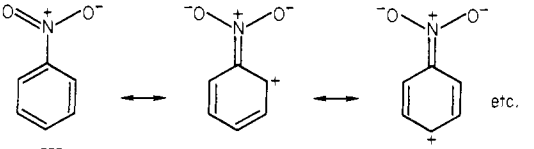
The effect of an amino substituent upon an aromatic ring is generally regarded as being a resultant of two opposing factors: an inductive withdrawal of electronic charge from the ring, coupled with a resonance donation of π charge to the ring.[1] The latter is commonly described by means of structures such as



I IIa IIb

Since it is observed experimentally that the presence of $-NH_2$ greatly activates the aromatic ring toward electrophilic attack (compared to benzene), it is concluded that the amine group is a strong π donor.[1]

In the case of the nitro group, on the other hand, both the inductive and the resonance effects are believed to result in the withdrawal of electronic charge from the ring, thus accounting for its observed deactivation toward electrophiles.[1] The resonance structures normally invoked include,



III IVa IVb

Thus, through both induction and resonance, $-NO_2$ is a charge acceptor. The inductive effect is the dominant one;[1-3] indeed it has recently been suggested that the role of structure IV may be very small.[4]

A quantitative measure of the relative roles of induction and resonance for these two substituents is given by their Taft constants, σ_I and σ_R.[5] For $-NH_2$, $\sigma_I = 0.13$ and $\sigma_R = -0.79$; for

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(5) The more positive is σ_I, the greater is the inductive electron-attracting tendency; the more negative is σ_R, the greater is the degree of electron donation through resonance. The quoted values are taken from: Wells, P. R. "Linear Free Energy Relationships"; Academic Press: New York, 1968; Chapter 2.

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